

Interim Technical Report No. 4/April 1, 1970 to January 31, 1971

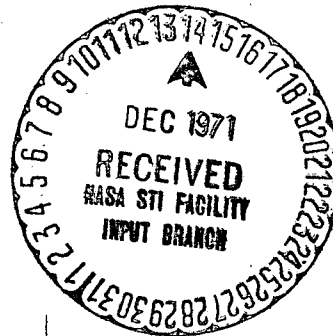
INDUCTION PLASMA CALCINING OF PIGMENT PARTICLES FOR THERMAL CONTROL COATINGS

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Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA 35812

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By: E. P. FARLEY

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Approved:

P. J. JORGENSEN, *Manager*
Ceramics Group

F. A. HALDEN, *Associate Director*
Physical Sciences (Materials)

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I INTRODUCTION

Zinc oxide (ZnO) is currently used as a pigment for thermal control coatings on space vehicles. Zinc orthotitanate (Zn_2TiO_4) has inherent qualities, such as a lower frequency ultraviolet absorption shoulder, that enhance its potential as a pigment. Both of these materials lose reflectance during space flights or space flight simulations because of ultraviolet radiation in vacuum. To decrease susceptibility to damage from ultraviolet radiation, the zinc oxide is coated with an alkali silicate, then heat treated at low temperature. Zinc orthotitanate is formed at temperatures between 900° and 1100°C . Unfortunately, both of these heat treatments cause sintering and particle agglomeration, and a subsequent comminution processing step must be employed. The comminution results in zinc oxide particles that are not completely coated with alkali silicate in one case, and zinc orthotitanate that is mechanically damaged, in the other. Therefore, a heat treatment that does not result in agglomeration and sintering, thereby eliminating the need for subsequent comminution of the pigment particles, should provide materials with greater resistance to ultraviolet radiation under vacuum conditions.

The plasma technique is an attractive method of calcining fine particles without producing sintered agglomerates. The objective of this study is to determine the potential of employing induction plasma heating techniques for calcining pigment particles used in thermal control coatings. Fine particles of silicated zinc oxide and zinc orthotitanate were dispersed in a carrier gas of argon and oxygen and were heated by hot argon produced in an induction plasma.

Work performed during previous report periods indicated that the plasma calcining process significantly improves the stability of thermal control coating powders. Work during this report period was primarily concerned with zinc orthotitanate.

II SUMMARY

During this research period, emphasis was placed on optimizing the calcination process. The plasma facility was completely rearranged in order to allow a closer and more detailed surveillance of process stages. The filter at the end of the system was replaced by an electrostatic separator, which allows better control of chamber pressure and a greater solid treatment capacity. The system was successfully operated at six times (3 grams/min.) the capacity employed in the past.

To overcome a serious time lag between pigment processing and obtaining test results from solar simulation, an attempt has been made to correlate electron paramagnetic resonance (EPR) spectra with simulation results. A series of specifically related test runs were made on one orthotitanate pigment. An optimum system temperature ($\Delta T = 1670^{\circ}\text{C}$) was chosen, on the basis of the results of a previous series of temperature settings. With this temperature as a reference point, the effective temperature at which the pigment was treated was varied 220°C in both directions. In addition to processing the pigment at various temperatures, we collected separate samples from each of four powder deposition areas within the system.

EPR spectra were obtained for each pigment sample collected. The spectra were taken at 300°K and 77°K . These samples were then exposed to vacuum UV radiation and EPR spectra were again obtained at 300°K and 77°K . All samples collected were subjected to solar simulation tests at IIT Research Institute.

A direct correlation exists between calcining parameters and the EPR changes observed within each sample series. There is also a correlation between vacuum-UV-initiated changes in EPR resonance peaks and the pigment's apparent susceptibility to irradiation damage in the solar simulator. At the present time, there are insufficient data to show a direct relationship between specific resonance peaks and specific damage modes.

One of the samples subjected to solar simulation exhibited the lowest vacuum-UV degradation at 2000 equivalent sun hours (ESH) ever

reported.

A preliminary test was run in which pigment material was recycled through the heat treatment. The results indicate that a longer dwell time at constant temperature would help achieve better vacuum UV stability.

The lag time in obtaining solar simulation data on the initial run with hafnia powder caused further testing on hafnia powders to be postponed until the next research period.

With the correlation now apparent between calcining parameters for orthotitanate pigments, EPR spectra changes, and solar simulator stability, modification of the plasma system becomes feasible in order to scale up the plasma processing operation to a larger pigment throughput.

III EXPERIMENTAL PROCEDURE

The experimental zinc orthotitanate (Zn_2TiO_4) pigments used in this investigation were produced at IIT Research Institute under NASA Contract No. NAS 8-5379. The preparation of the Zn_2TiO_4 pigments has been described in earlier reports.^{1,2,3} In addition, a hafnia powder sample was submitted to SRI by NASA, Huntsville.

To maintain continuity in the test series run during this research period, one specific Zn_2TiO_4 pigment was employed in all sets. This pigment was designated as SRI Sample No. 10 (IITRI Sample No. B 296). It reportedly was fired at 925°C for 18 hours with 0.5% excess ZnO in its formulation, and was given a silicate and phosphate surface treatment followed by dry ball milling. The hafnia sample was a physical mixture of 95% HfO_2 and 5% CaO, and was prepared by Dr. John Buckley, Langley Research Center.

The plasma apparatus used in this study was described in detail in Interim Technical Report No. 1,¹ and the present operating conditions were described in Interim Technical Report No. 2.² With one exception all runs were conducted at pressures between 11 and 15 torr. The pigments were injected downstream from the plasma. The constant gas flow rate employed produces a constant residence or heating time of about 1.1 seconds. The gas temperature in excess of ambient (ΔT) is calculated from the gas flow rate, the input electrical energy, and the heat capacity of the argon plasma gas, and is given by equation (1)

¹R. W. Bartlett, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 1, PMU-7083, (August 15, 1968).

²E. P. Farley and P. J. Jorgensen, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 2, PMU-7083 (July 30, 1969).

³G. A. Zerlaut and N. A. Ashford, "Development of Space-Stable Thermal-Control Coatings," IITRI Triannual Report No. IITRI-46002-85 (February 20, 1970).

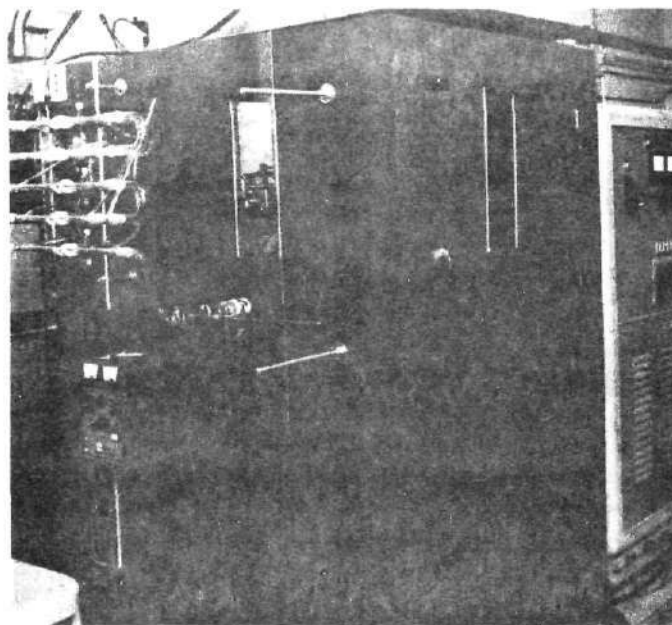
$$\Delta T = 25 E_p I_p / J \quad (1)$$

where J is the total gas flow rate in liters/min at S.T.P., E_p is plate voltage, and I_p is plate amperage. The constant in this equation accounts for the conversion of units and the plasma efficiency. The plasma consisted entirely of argon, whereas the gases used to transport the pigment particles into the plasma apparatus contained equal amounts of argon and oxygen. The total resulting gas composition in the reactor was 80.7% argon and 19.3% oxygen.

During this research period the physical arrangement of the calcining facility was completely altered to allow better observation and the isolation of the processed pigments from the intense UV radiation of the plasma flame. Figure 1(a) shows the walled enclosure built around the RF work coil and quartz reaction chamber. Two UV-safe windows were located 90° apart to offer full observation of the quartz reaction chamber. The first condenser extends out through the wall to the remainder of the collection system. This effectively isolates the pigment particles deposited in the last two collection zones from UV radiation produced by the plasma flame.

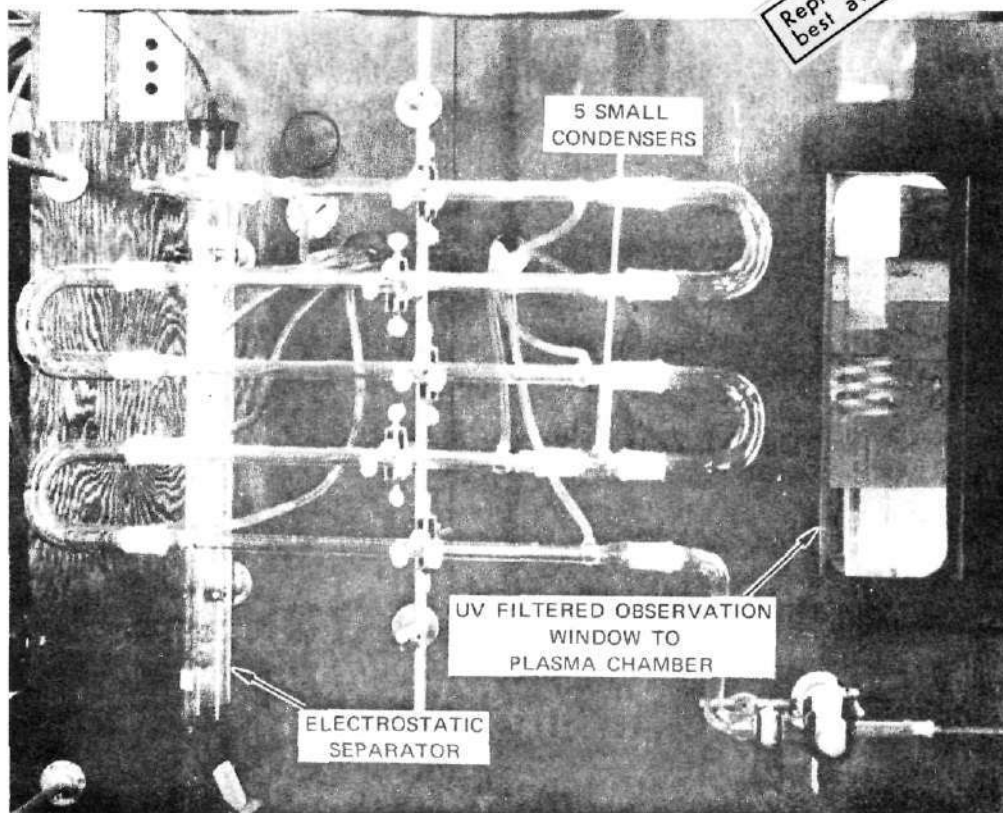
In the past, the system included a filter at the end of the collection train. The system was operated at a slight negative pressure (633 and 710 torr). At a 1/2 gram/minute feed rate, the filter would quickly fill and result in relatively short runs and large downtime to change filters. To increase capacity and length of runs, the small condensers were arranged in series (Fig. 1b) with the powders flowing upward through the assembly. This increases powder contact with the condenser walls and enhances deposition within the condenser bank. The original filter was replaced with an electrostatic separator, that eliminated the buildup of back-pressure and allowed more controlled and consistent operating conditions.

After processing, the starting materials and the calcined products were analyzed by x-ray diffraction, scanning electron microscopy (SEM), Fisher sub-sieve analysis, and electron paramagnetic resonance (EPR). The materials were then submitted to IITRI for solar simulation and



(a) COLLECTION SYSTEM OUTSIDE PLASMA AREA
AND SHIELDED FROM UV RADIATION

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(b) NEW CONDENSER SYSTEM FOLLOWED BY
ELECTROSTATIC SEPARATOR

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FIGURE 1 PLASMA CALCINING FACILITY

spectroreflectometry.

The EPR tests were run on the system described in Interim Technical Report No. 3⁴ with a modification in the sample-holding system that prevented oxygen contamination. In the previous ESR studies the powdered samples were sealed in a quartz tube after a vacuum heat treatment designed to remove any adsorbed gases. The seal-off procedure and the subsequent UV irradiation in this closed, low volume system could have introduced an ambient gas pressure that would inhibit photodegradation.

In the present series, provision was made to more closely approximate the space environment by maintaining a low pressure during irradiation as well as during ESR measurements. This was achieved by attaching the quartz tube (3 mm i.d.) holding each sample to a Vac-Ion pump (Varian, 2 l/s). The samples were evacuated with a standard vacuum system (oil diffusion pump with liquid nitrogen traps) and heated at 150°C for 18 hours. The sample system was then sealed off from the pump-out system leaving only the Vac-Ion pump in operation. The ambient pressure was subsequently maintained at about 10^{-8} torr, but it increased during irradiation to about 10^{-7} torr.

A high pressure mercury arc (PEK-200) was employed as an irradiation source and was positioned at a distance of 23 inches from the sample. The sample was not rotated during irradiation because of the attached Vac-Ion pump.

The ESR measurements were made before and after irradiation time of one hour and at two temperatures, 300° and 77°K. The instrumental gain at 300°K was five times larger than at 77°K; that is, the spectra were weaker at 300°K.

Since temperature equilibration was very slow because of the low pressure, one hour was allowed for the equilibration.

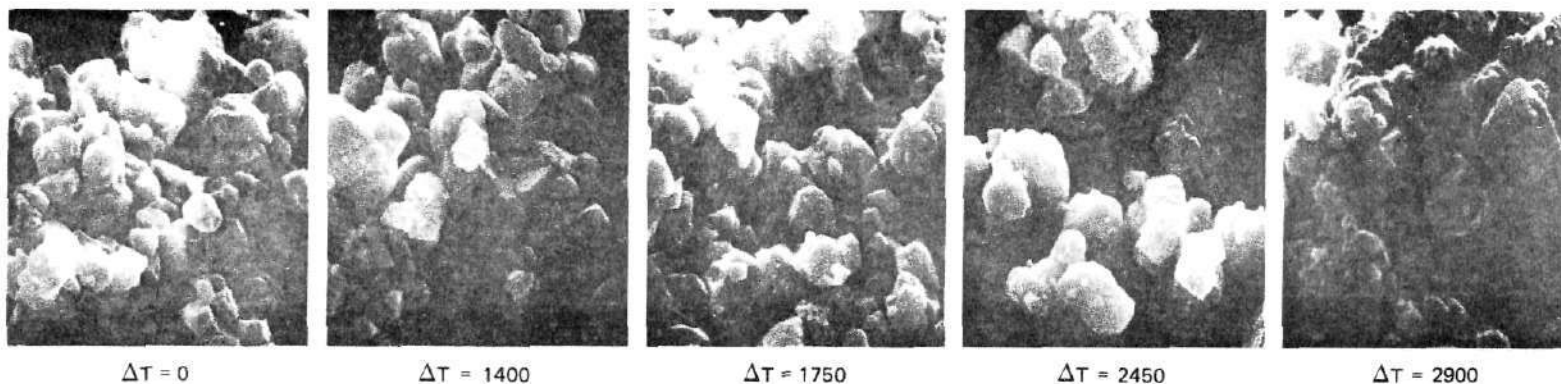
⁴E. P. Farley, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 3, PMU-7083 (May 8, 1970).

IV RESULTS AND DISCUSSION

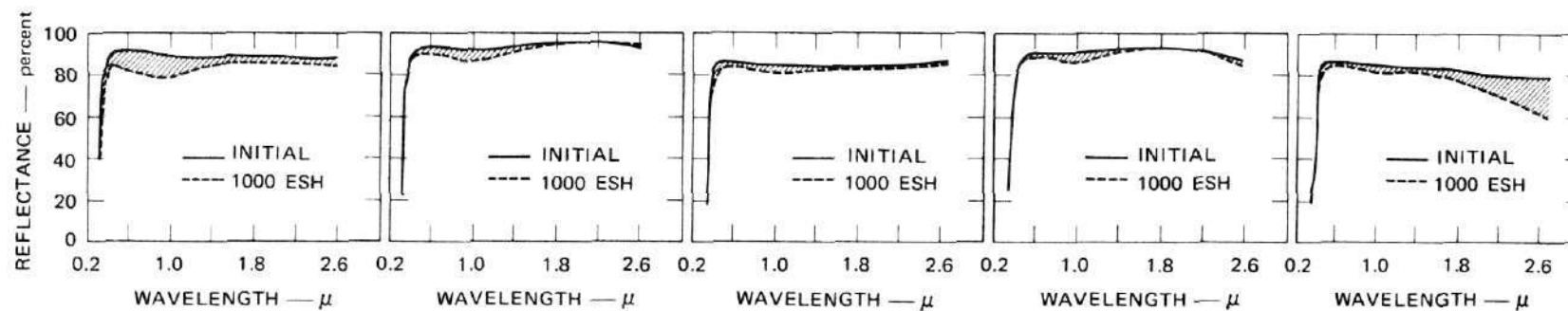
A. Plasma Calcining

In the last research period, covered in the Interim Technical Report No. 3,⁴ three different Zn_2TiO_4 pigment powders were subjected to two different calcining temperatures. The effect of calcining was determined by characterizing the powders before and after heat treatment. Changes were observed in the EPR spectra and reflectance and in the development of free zinc oxide at high temperatures. Two additional products of one pigment (SRI No. 3) were produced at two different temperatures to set up a temperature series with four points (1400, 1750, 2450, and 2900°C). These were submitted for solar simulation, and the results were available at the beginning of this research period. The resulting series characterized in Fig. 2 indicated that an optimum calcining temperature lay between 1400 and 1750°C and probably closer to the latter. With this information as a guide, an intermediate temperature (1670°C) was chosen as a reference point. A new three-point temperature series was then run at the reference point and 220°C on both sides of it. With the new system modifications, a sufficient quantity of pigment was produced to permit a thorough characterization of the products. The effect of varying the chamber temperature is illustrated in Fig. 3, showing the changes in reflectance spectra before and after vacuum UV irradiation. After 2000 equivalent sun hours, (ESH) the pigment treated at 1670°C exhibits higher stability than either of the others.

In the past it was noted that there was a significant difference in pigment powders deposited in different areas of the plasma calcining system. With the larger capacity of the new system, each run was continued until a sufficient quantity built up in each of the four collection areas: (1) reaction chamber, (2) first condenser, (3) small condenser bank, and (4) electrostatic separator. The nature of these products is illustrated in Fig. 4. The samples differ mostly in particle size.



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FIGURE 2 EFFECT OF CHAMBER TEMPERATURE ON PARTICLE MORPHOLOGY AND UV RADIATION STABILITY AS INDICATED BY CHANGE IN REFLECTANCE SPECTRA

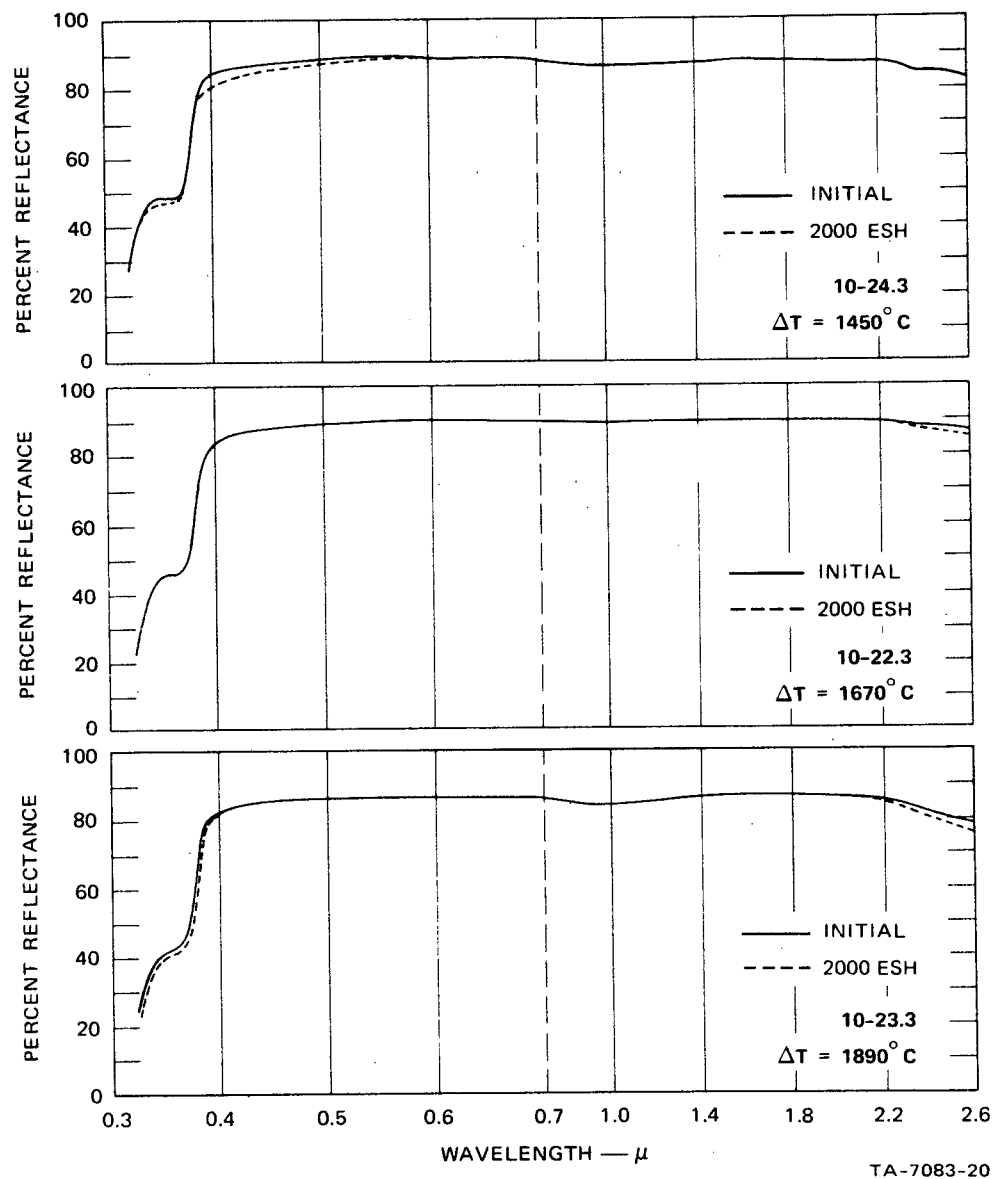
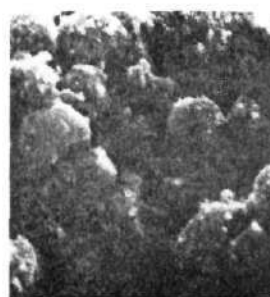
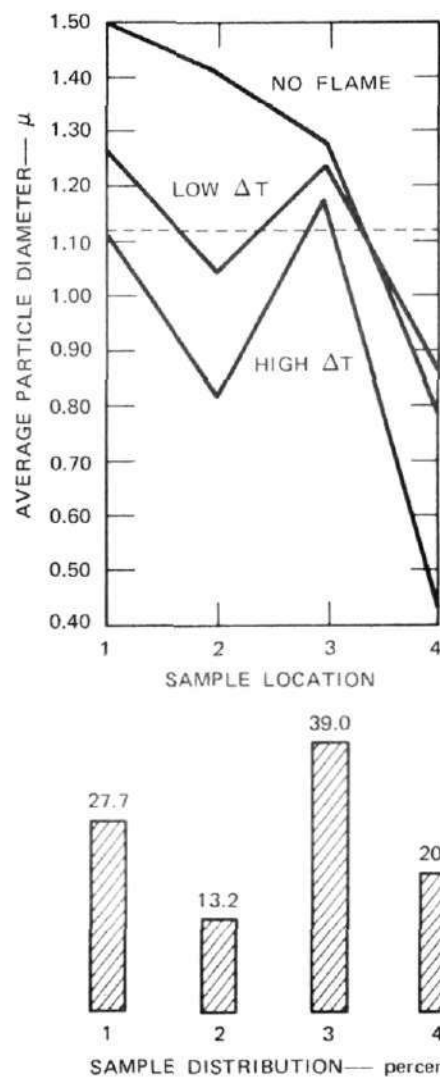
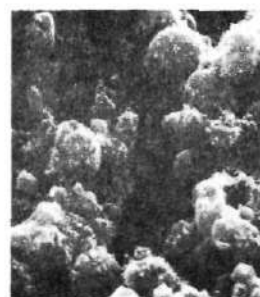


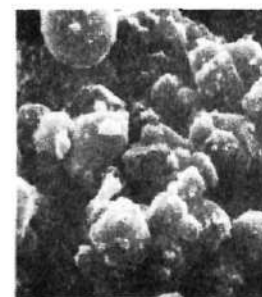
FIGURE 3 EFFECT OF CHAMBER TEMPERATURE ON REFLECTANCE SPECTRA BEFORE AND AFTER VACUUM UV IRRADIATION (2000 ESH EXPOSURE)



1



2



3



4

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1



2



3



4

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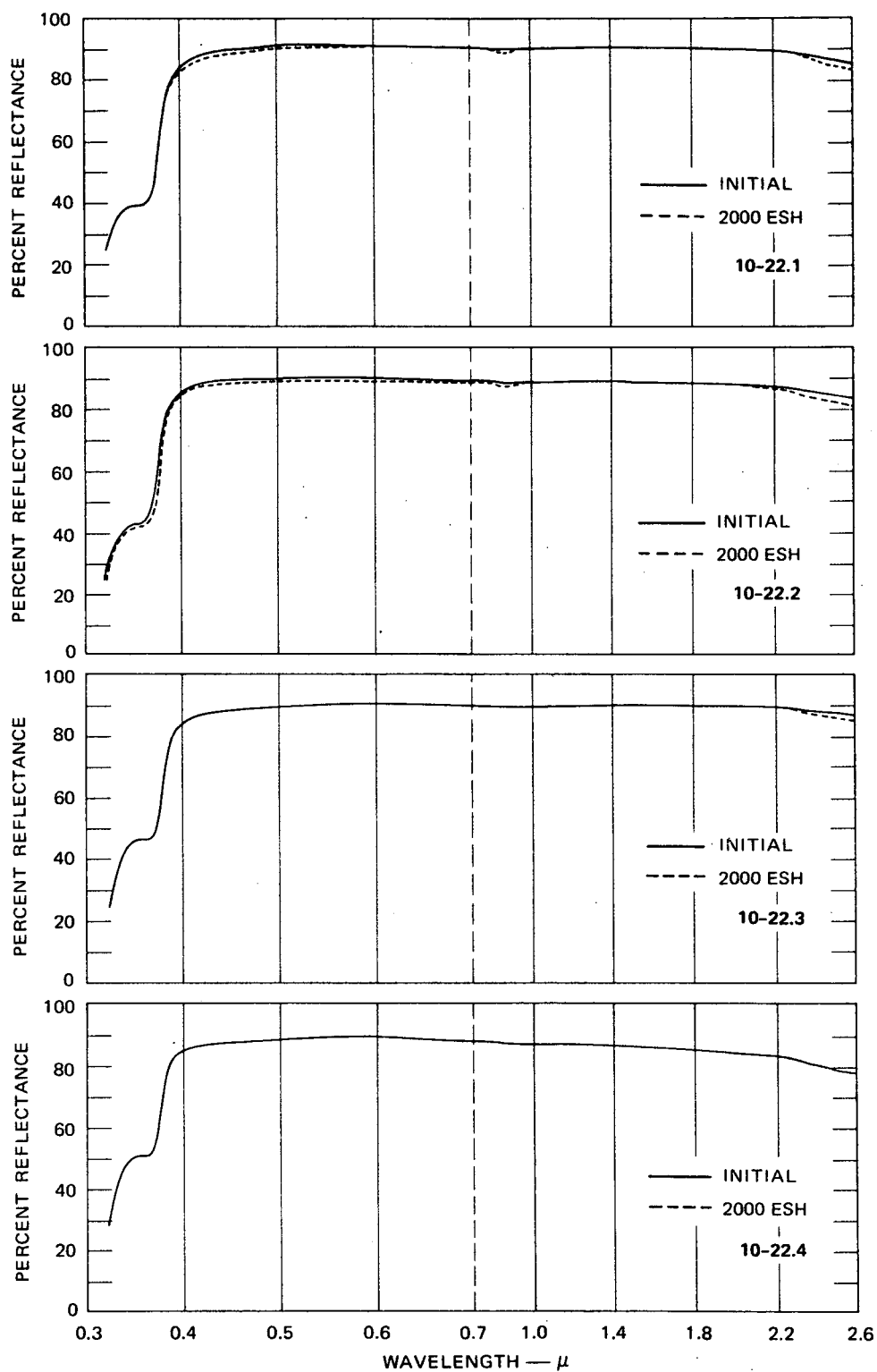
FIGURE 4 EFFECT OF SAMPLE COLLECTION POINT ON PARTICLE SIZE DISTRIBUTION

A small secondary phase tends to accumulate in the second and fourth areas. If no heat is applied to the system, there is a consistent decrease in particle size from area (1) through area (4). The weight distribution graph shows that the majority of the material accumulates in the reaction chamber (1) and in the small condenser bank (3). Samples from each area after calcining at 1670°C were submitted for solar simulation. Figure 5 illustrates the changes in reflectance spectra before and after vacuum UV irradiation. The sample from the electrostatic separator exhibits the highest stability after 2000 equivalent sun hours ever reported to date for a zinc orthotitanate pigment.

The relationships among the samples from three test series are illustrated in Fig. 6, which shows the distribution of crystalline phases among the various products. Secondary phases are just barely discernible in the diffraction patterns. The starting materials show three distinct peaks at "d" values of 4.27, 3.87, and 3.33. After heat treatment, two of these are replaced by peak values of 4.39 and 4.10. These peaks appear to be associated with the silicate and phosphate surface treatment, but do not correspond with any compounds listed in the ASTM file. The volatility of the surface coating material is demonstrated by the coloration of the plasma tail flame surrounding the incoming powder particles (Fig. 7). The apparent volume of the coloration was directly related to chamber temperature. The higher the temperature, the brighter and longer the length of coloration. It is apparent from the X-ray diffraction patterns that the secondary crystalline phase has disappeared in all electrostatic separator samples. A separate test, which was carried out at a slightly higher chamber pressure (Fig. 6), exhibited almost no secondary phases in all four collection areas, yet the apparent stability of the area 3 product from each series is almost identical (Fig. 8).

B. Electron Paramagnetic Resonance (EPR)

The EPR studies were enlarged to develop any correlation between Zn_2TiO_4 paramagnetic resonance activity and the pigment's susceptibility to vacuum UV damage as indicated by changes in reflectance spectra. At resonance, microwave energy is absorbed by the sample. The amount of

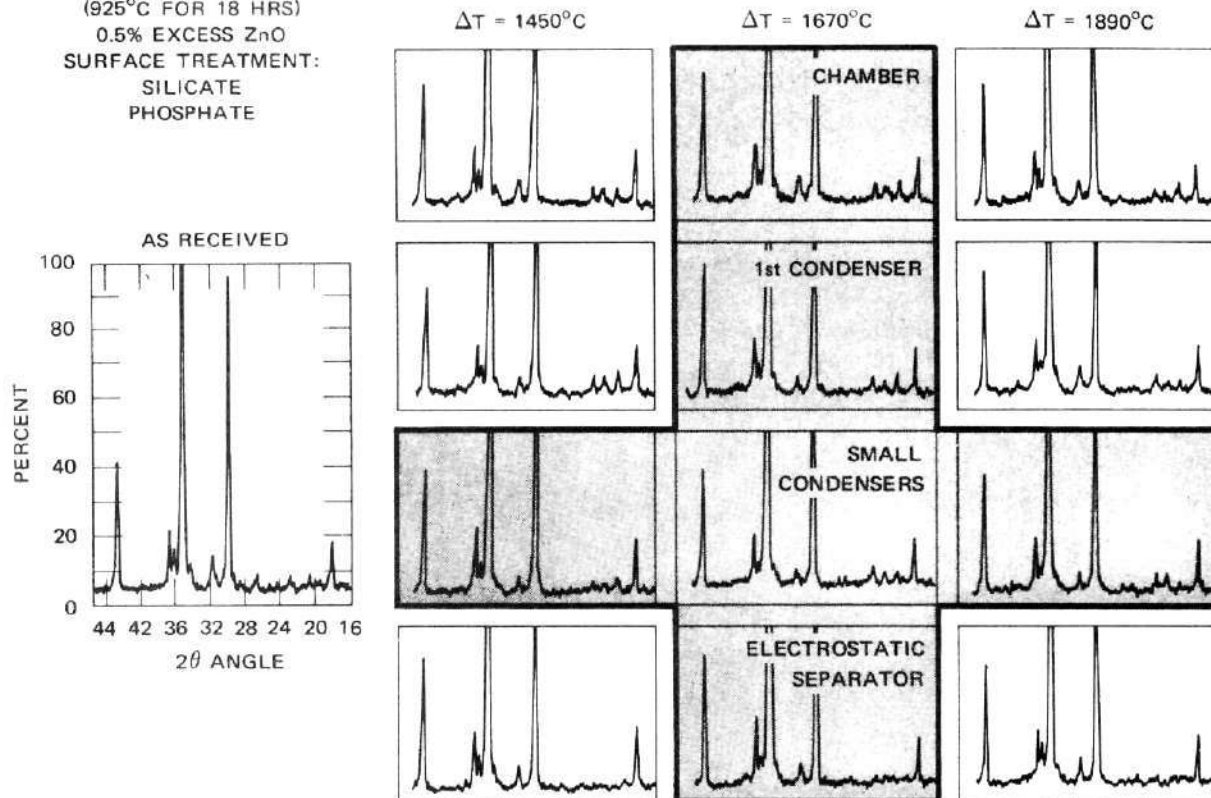


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FIGURE 5 EFFECT OF SAMPLE COLLECTION POINT ON REFLECTANCE SPECTRA BEFORE AND AFTER VACUUM UV IRRADIATION (2000 ESH EXPOSURE) ($\Delta T = 1670^{\circ}\text{C}$)

ZINC ORTHOTITANATE (Zn_2TiO_4)
 (925°C FOR 18 HRS)
 0.5% EXCESS ZnO
 SURFACE TREATMENT:
 SILICATE
 PHOSPHATE

CHAMBER PRESSURE = 11 TO 15 mm Hg



CHAMBER PRESSURE = 32 mm Hg

$\Delta T = 1670^\circ\text{C}$

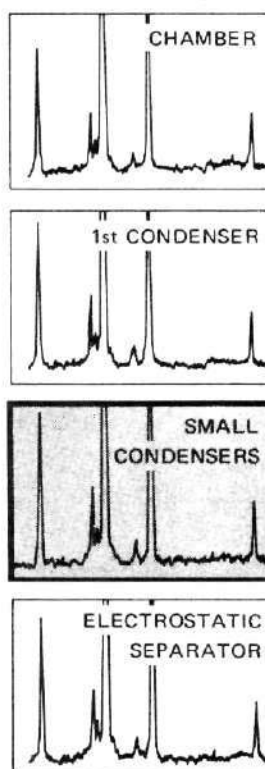
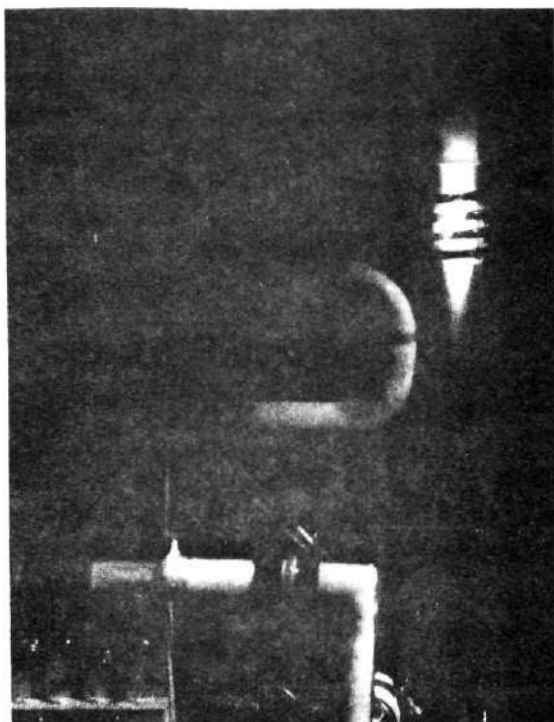


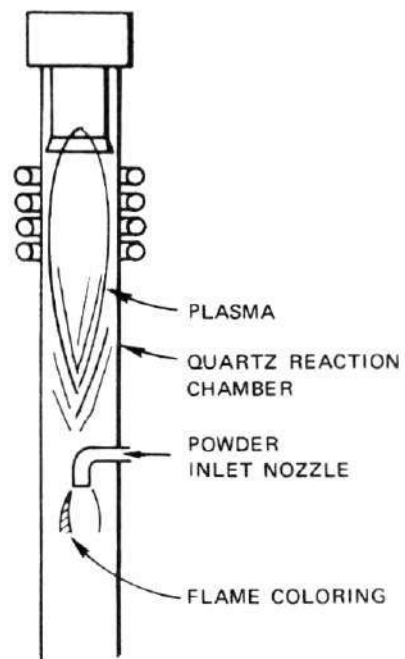
FIGURE 6

EFFECT OF CHAMBER TEMPERATURE,
 CHAMBER PRESSURE AND SAMPLE
 LOCATION ON CRYSTALLINE PHASES
 PRESENT IN SILICATE AND PHOSPHATE
 COATED Zn_2TiO_4

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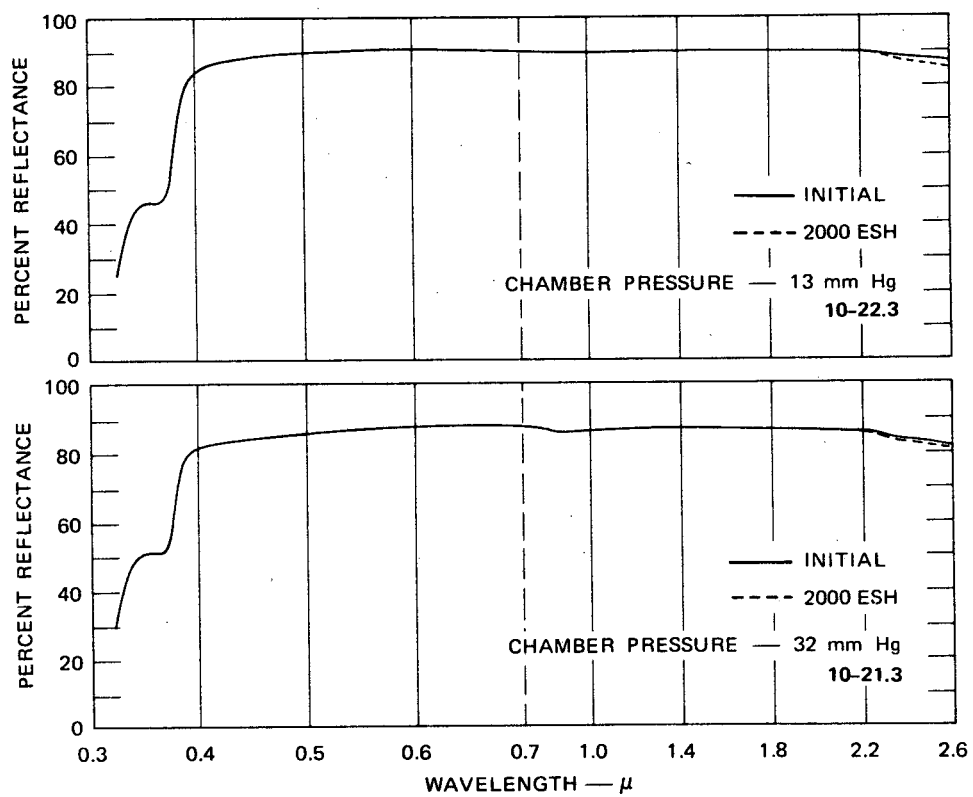
HEAD-ON VIEW



SIDE VIEW

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FIGURE 7 COLORING IN PLASMA TAIL FLAME DUE TO PRESENCE OF SILICATE AND PHOSPHATE COATING ON PIGMENT PARTICLES



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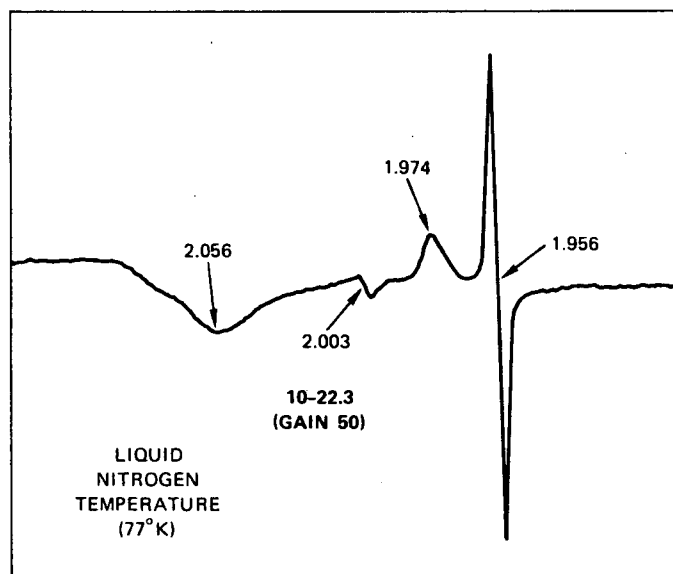
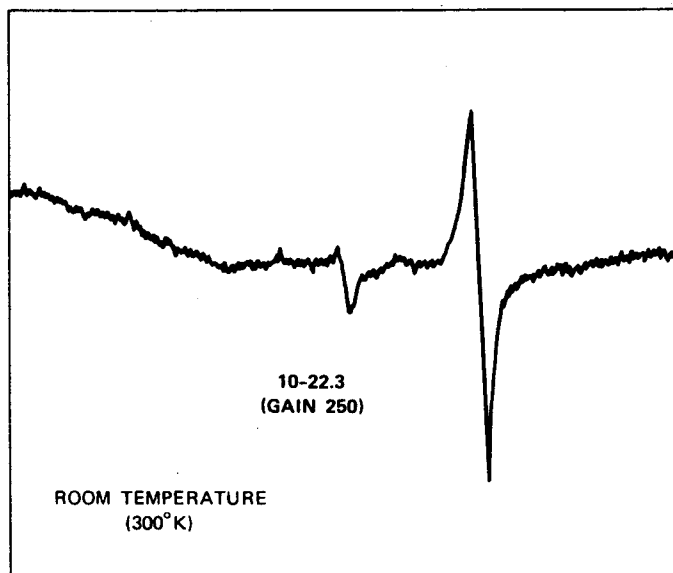
FIGURE 8 EFFECT OF CHAMBER PRESSURE ON REFLECTANCE SPECTRA BEFORE AND AFTER VACUUM UV IRRADIATION (2000 ESH EXPOSURE)

absorption is proportional to the number of paramagnetic electrons and depends on the difference in population of the upper n_+ and lower n_- states according to

$$n_+ = n_- \exp\left(\frac{\Delta E}{kT}\right) \quad (2)$$

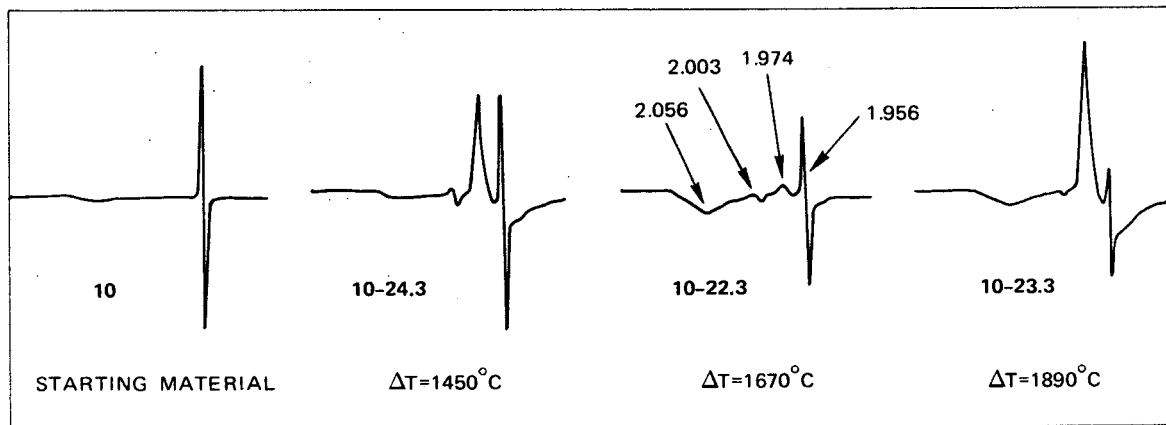
where k is the Boltzman constant, and T is the absolute temperature. Equation (2) indicates that the sensitivity for detection of paramagnetic electrons is greater at lower temperatures where the population is greater. Some EPR peaks present at low temperature will disappear at higher temperatures. To fully characterize the pigment powders, spectra were made both at 300°K and 77°K. For comparison, Fig. 9 illustrates the spectra at both temperatures. The EPR spectra contained four resonances: (1) the resonance (y) at $g = 1.956$ is typical of donors in ZnO. In pure ZnO irradiated under similar conditions, the intensity of this resonance increases markedly upon UV irradiation; (2) resonance (x) at $g = 1.974$ is assigned to Ti^{+3} species. The resonance is not as apparent at the high temperature because line broadening occurs; (3) the resonance at $g = 2.003$, typical of a "free" electron, could be due to several types of paramagnetic centers. For example, such a resonance is found in samples containing free radicals, carbon, F-centers, and dislocations; (4) the resonance at $g = 2.056$ also cannot be assigned at this time, however it is probably due to a transition metal impurity such as iron.

It is evident from Fig. 9, with the exception of the resonance at $g = 2.003$, that the liquid nitrogen spectra are more definitive in peak height; therefore, to illustrate the EPR spectral relationship between the various pigment samples only the liquid nitrogen spectra have been used. Figure 10 shows the spectra resulting from the temperature series. Resonance 1.956 shows a constant decrease in peak height as the temperature increases. Resonance 1.974 exhibits a rather surprising minimum at 1670°C. Resonance 2.003 again demonstrates a decrease with increasing temperature. The broad peak at $g = 2.056$ shows an opposite reaction to resonance 1.974 in that it goes through a maximum at 1670°C. Figure 11 illustrates the spectra at two chamber pressures when samples are collected from each of the deposit areas. The differences observed between the various spectra



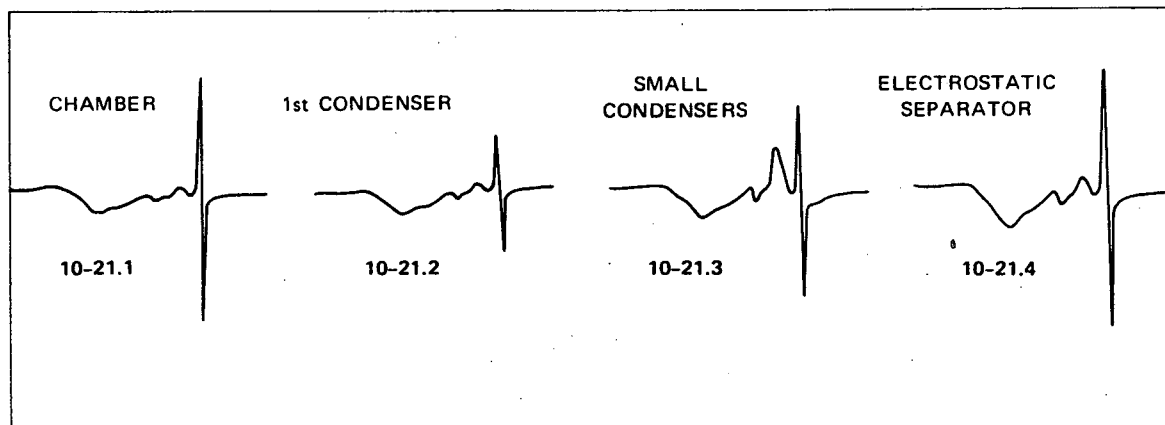
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FIGURE 9 EFFECT OF EPR CAVITY TEMPERATURE ON PEAKS

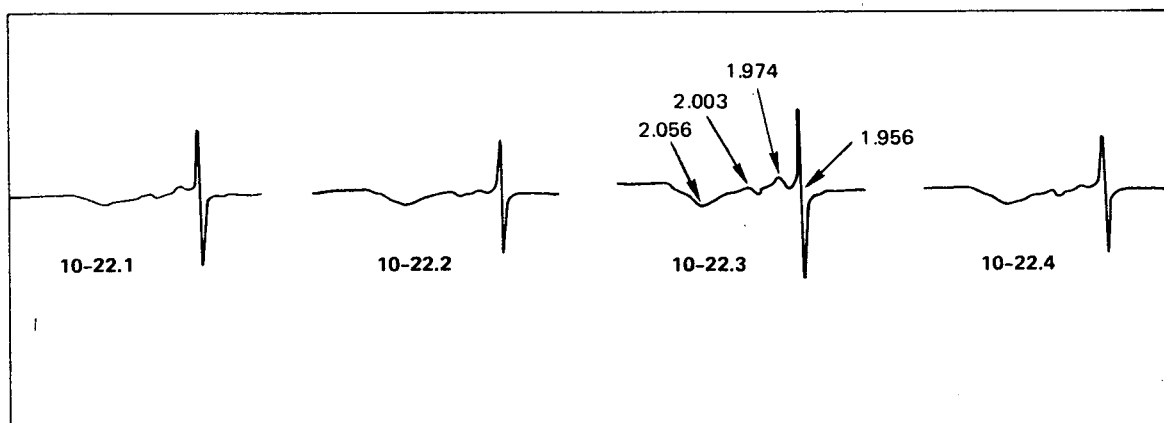


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FIGURE 10 EFFECT OF CHAMBER TEMPERATURE ON EPR PEAKS



CHAMBER PRESSURE (P_2) — 32 mm Hg



CHAMBER PRESSURE (P_2) — 11 to 15 mm Hg

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FIGURE 11 EFFECT OF SAMPLE COLLECTION POINT ON EPR PEAKS

are probably related both to thermal history and particle size. Fisher analysis of average particle size for run 23 gave the following:

<u>Sample</u>	<u>Collection Location</u>	<u>Avg. Particle Diam. (μm)</u>
10-23.1	Reaction chamber	1.57
10-23.2	First condenser	1.27
10-23.3	Small condenser bank	1.45
10-23.4	Electrostatic separator	0.82

These values compare well with past experience. The average particle size of the starting material was 1.45 micrometers in diameter. These size values have no relationship to actual grain size in that the Fisher analysis does not distinguish agglomerates. SEM photos show the grain size to be closer to 0.8 micrometers.

When a comparison is made between changes in EPR resonance peak heights before and after UV irradiation, a correlation can be drawn between these changes and solar-simulation-induced changes in reflectance spectra. To illustrate the changes produced by vacuum UV irradiation in the EPR spectra, the peak heights were all adjusted to a gain of 50 and plotted in millimeters of height (Fig. 12). A splitting of the plotted line for a given resonance is a direct reading of the degree of change produced by one hour of exposure to the mercury arc. Where the lines converge there was no apparent effect of UV radiation on that particular EPR resonance. The graphs of both sample series are plotted on a log scale. This helps to illustrate the $\frac{1}{T}$ temperature effect on the 1.956 and 1.974 resonances between 300^oK and 77^oK. The resonance at 2.003 is anomalous in this respect and no explanation is evident at this time. When these two graphs are compared with the solar simulation results in Fig. 3 and Fig. 5, it is evident that the samples that show changes in EPR peak-height correspond to the samples that showed changes in reflectance spectra during solar simulation. Thus, the EPR examination appears to provide an easily accessible tool for measuring the effects of changes in plasma calcination processing parameters.

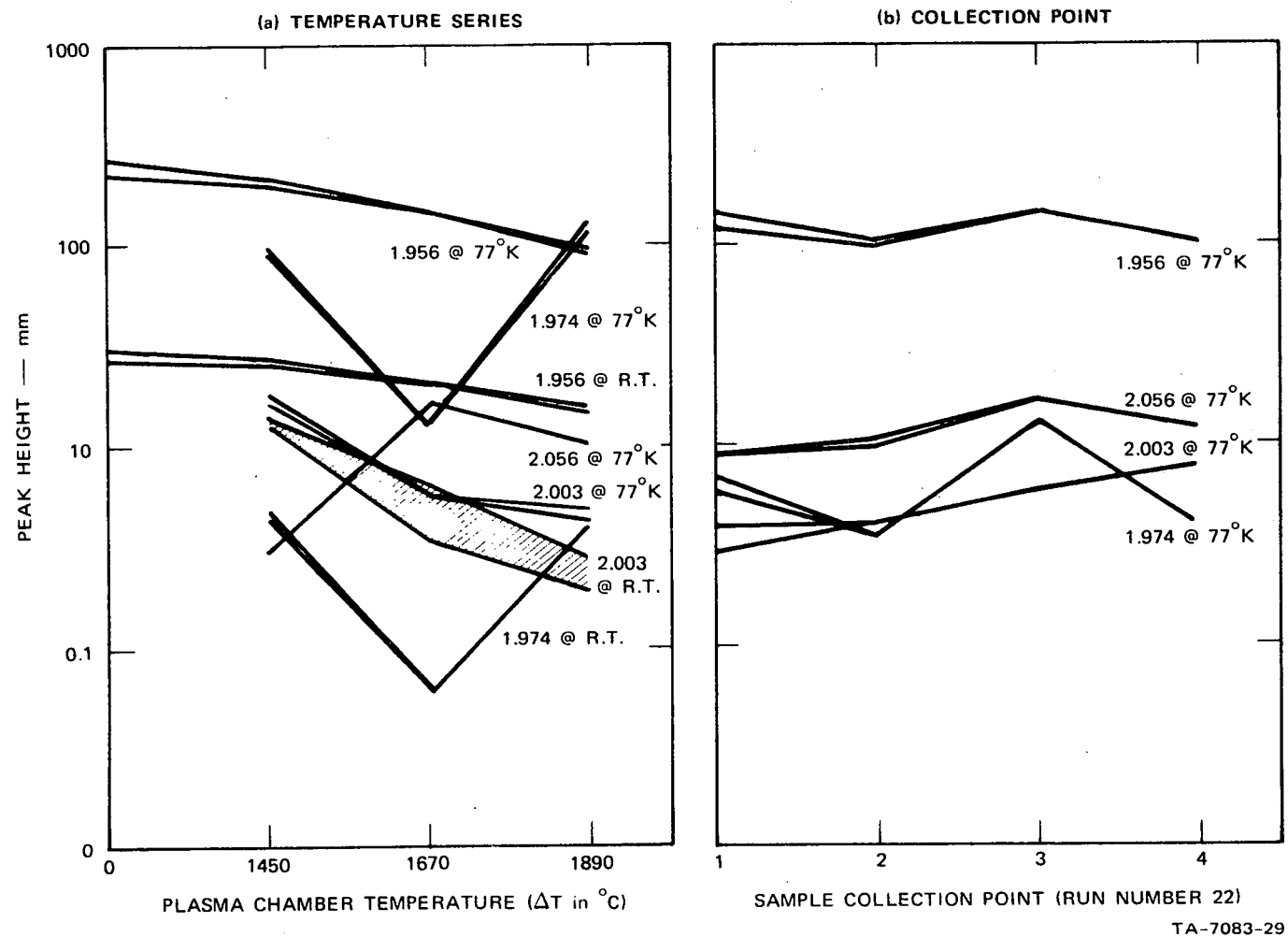


FIGURE 12 EFFECT OF VACUUM UV IRRADIATION ON EPR PEAK HEIGHT

C. Multiple Pass Experiment

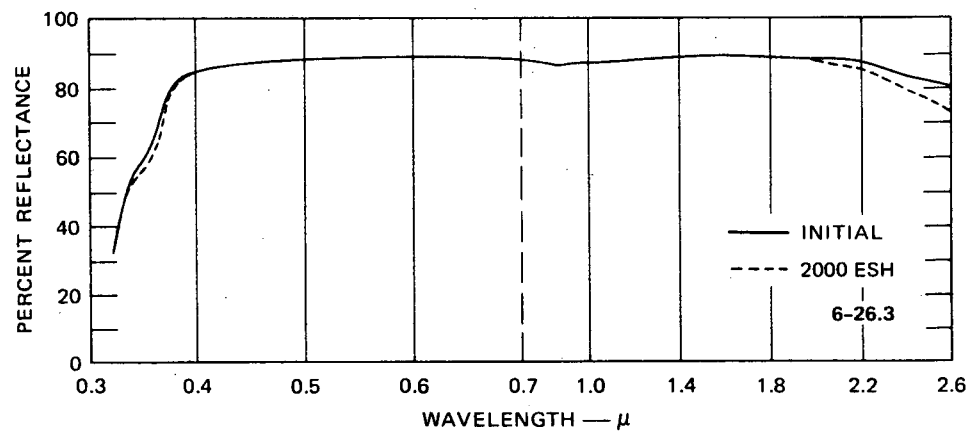
To check the effect of dwell time on the calcining process, a test was run in which a pigment was passed through the plasma system twice. The Zn_2TiO_4 pigment was chosen on the basis of availability of a sufficient quantity of material and reasonable stability. The pigment is from last year's group and is designated as SRI Sample No. 6. This pigment reportedly was formed at 925°C for 18 hours; the excess ZnO was extracted; the pigment was then refired at 1050°C for 5 hours, and finally ball milled for 24 hours. This pigment, when calcined at $T = 1950^\circ\text{C}$, indicated very good stability (Interim Technical Report No. 3) for uncoated Zn_2TiO_4 .

The pigment was run through the plasma system at the reference temperature ($T = 1670^\circ\text{C}$) and a sample was taken from the small condenser bank (6-26.3). The remainder of the small condenser bank material was then recycled at the reference temperature. A sample was again collected from the small condenser bank (6-27.3). This last sample was too small to submit to solar simulation but was sufficient for EPR analysis. The one-pass material was submitted to IITRI; Fig. 13 shows the reflectance spectra after 2000 ESH. The stability is still not as good as that of the coated pigments but is considerably better than that of the original sample run at 1950°C . The low temperature spectra before vacuum UV irradiation of each sample is shown in Fig. 14. The changes in EPR spectra after UV treatment indicate the second pass sample to be significantly more stable than the single pass material. This indicates a need for longer dwell times in the plasma chamber. This could be achieved through physical modification of the fluid flow characteristics of the reaction chamber.

D. Hafnia Sample

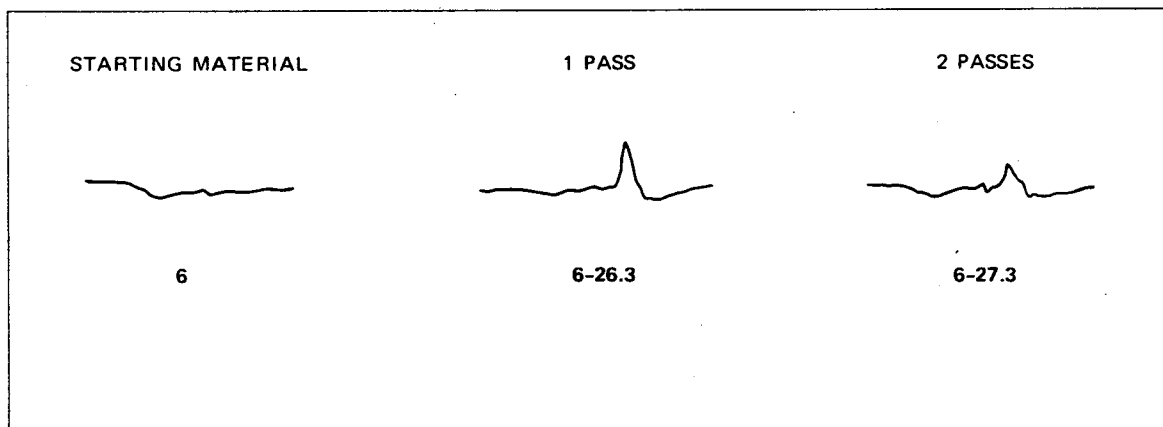
The hafnia-calcia mixture was submitted to a calcining temperature of 2120°C and the small-condenser product was X-rayed (Fig. 15) and a sample was sent to IITRI for solar simulation testing. Since the data on this preliminary run (Fig. 16) returned too late to make any additional plasma runs, further treatment studies will be carried out during the next research period. The only effect of calcination observed in X-ray patterns was the apparent concentration of CaO in the small condenser bank product. The

degradation produced in solar simulation seems to be only at the UV end of the spectrum.



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FIGURE 13 EFFECT OF REFERENCE CHAMBER TEMPERATURE ($\Delta T = 1670^\circ\text{C}$) ON STOICHIOMETRIC Zn_2TiO_4 PIGMENT



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FIGURE 14 EFFECT OF MULTIPLE PLASMA CALCINING PASSES ON EPR PEAKS

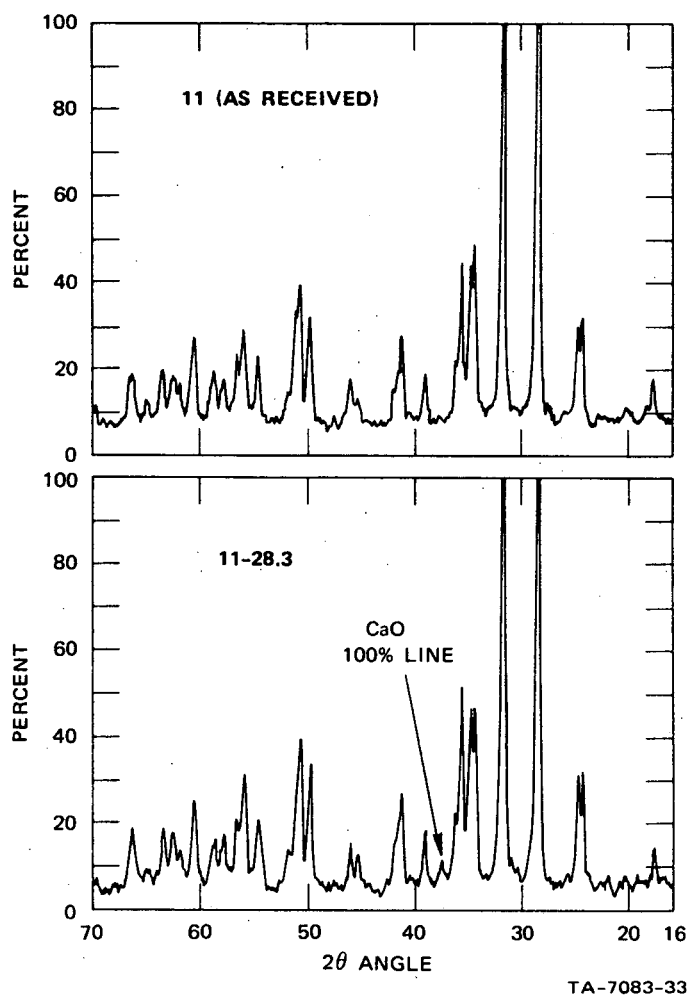


FIGURE 15 X-RAY PATTERNS OF $\text{HfO}_2 + \text{CaO}$ MIXTURE BEFORE AND AFTER PLASMA CALCINING @ $\Delta T = 2120^\circ \text{C}$

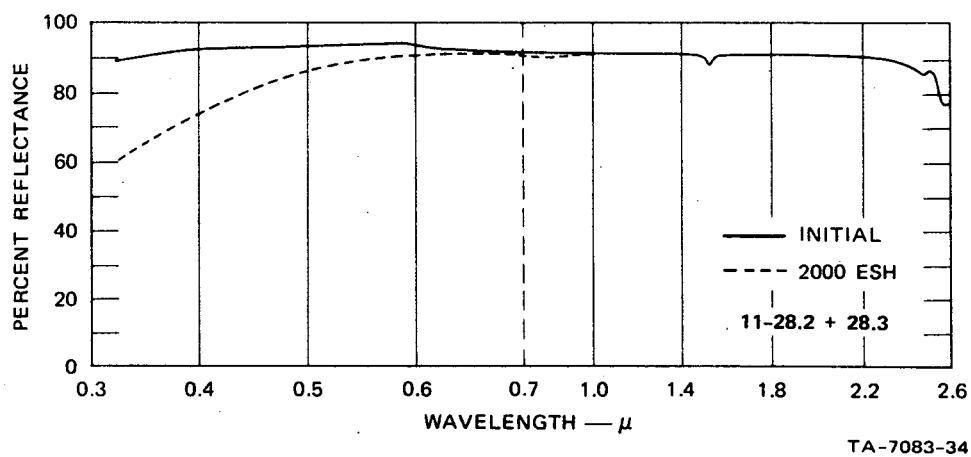


FIGURE 16 REFLECTANCE SPECTRA OF CALCINED $\text{HfO}_2 + \text{CaO}$ MIXTURE BEFORE AND AFTER VACUUM UV IRRADIATION (2000 ESH EXPOSURE)

V FUTURE WORK

During the next research period the following areas should be considered for investigation:

1. The effect of residence time. This will be examined by multiple passes or through modifications to the reaction chamber transport and mixing characteristics.
2. Reactive plasma environments. This is to provide improved stability of coating materials.
3. New pigments systems. The hafnia sample introduced during the present research period will be given additional treatment.

The correlation established between EPR and reflectance changes due to vacuum UV irradiation should allow for quick evaluation of the first two areas.

VI ACKNOWLEDGMENTS

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